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TITLE: HEAVY-ELECTRON MATERIALS

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Heavy-Electron Materials

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1. Introduction

The earmark of the intermetallic compounds known as heavy-Fermion or heavy-electron materials is a low temperature linear electronic specific-heat coefficient (γ) which shows an upturn on cooling to low temperatures, typically below 4 K (Fig. 1). It is clear from data on the gap anomaly of heavy-electron superconductors that this γ is of electronic origin and, further, that f-electrons must have something to do with it. Only the 4f and 5f elements, typically thought of as forming valence-fluctuation compounds (mainly Ce, Yb, U, and Np) seem to also form heavy-electron compounds. We list a number of these heavy electron compounds in Table 1.

All the heavy-electron compounds have magnetic susceptibilities which are Curie-Weiss-like at high temperature, with effective moments close to that of their expected f-configurations. At low temperature this susceptibility becomes Pauli-like, showing no tendency to saturate even for large H/T (magnetic field over temperature). One way to think about this is in Kondo terms: at high temperature we have local moment behavior, while on cooling to low temperature these local moments are compensated by a screening cloud of conduction electrons, the resulting low temperature state of the lattice being a Fermi liquid involving coherent, Bloch electron states. The plot of $\gamma(o)$ versus $\chi(o)$ (Fig. 2) shows all the data below the Sommerfeld line, the line for which, loosely speaking, all the χ shows up in γ.

This Kondo viewpoint allows a qualitative estimate of γ. Suppose the crystal-field ground state of the f-level is a doublet. The kln2 entropy of this doublet will disappear upon the establishment of the low temperature coherent state and must therefore appear in the conduction electron entropy. If the compensation has a characteristic temperature T_o, then we estimate $\gamma \sim R\ln 2/T_o = 5.76/T_o$ J/mole-K^2.

Hall-effect data give further useful information. Studies of a number of heavy-electron compounds [1,2] show that at high temperatures there is a large, positive contribution to the Hall constant which is lost upon the establishment of coherence. While the temperature variation of the Hall-effect is not here understood in detail, the gross effects are [3,4]: incoherent skew scattering from the impurity-like f's at high temperature makes a large, positive contribution to the Hall constant. This scattering disappears upon the establishment of coherent Bloch states at low temperature (Fig. 3). The extra insight derived from the Hall data is that compounds such as $CePd_3$, whose $\gamma = 37$ mJ/mole Ce-K^2 [5] and is not normally thought of as a heavy-electron material, also show the temperature dependence in their

Hall constants, only here T_o is much larger.

The Hall data then allows us to hope that there is possibly a whole continuum in the physics linking typical transition metal γ's of 10 mJ/mole-K^2 with the heaviest electron γ's over 1 J/mole-K^2. Thinking in band-structure terms, as the bands become narrower and γ increases, electron correlations lead to even narrower effective bands, where the Anderson Hamiltonian is appropriate. The simple viewpoint presented above is clearly not applicable over the whole range of variation of γ; our point is that the underlying physics may not change as drastically as γ does. We note that recent de Haas-van Alphen results on the compounds $CeCu_6$ [6] and UPt_3 [7] confirm the large masses expected, demonstrate the existence of a Fermi surface at sufficiently low temperature, and show that the entire Fermi surface involves heavy electrons.

2. Superconductivity

We turn now to the phase transitions in this heavy-electron state observed at low temperatures. These are either magnetic or superconducting. Some compounds (e.g. $CeAl_3$, $CeCu_6$, $UAuPt_4$) do not show a co-operative low temperature phase transition, and, to date, no charge density wave transition has been identified in these materials. We deal first with the superconductors.

There are three known examples of heavy-electron superconductivity: $CeCu_2Si_2$ (T_c = 0.6 K) [8], UPt_3 (T_c = 0.54 K) [9] and UBe_{13} (T_c = 0.9 K) [10]. The specific heat plotted as C/T versus T^2 is shown in Fig. 1 for UBe_{13}. The anomaly at T_c is very much in the strong-coupling regime, and it demonstrates, in fact, that the superconducting gap opens in the heavy quasiparticle band. This shows that γ really does represent the electronic density of states. The specific heat anomalies at T_c for $CeCu_2Si_2$ and UPt_3 are generally somewhat smaller than weak coupling BCS theory and very dependent on sample quality. The accurate fit of the low temperature normal state specific heat of UPt_3 to the spin fluctuation form $T^3 \ln T$ led to an early suggestion that paramagnon exchange might be the mechanism producing its superconductivity [9].

The special interest in the superconductivity of the heavy-electron materials is that both a new type of pairing and/or a new mechanism may be involved. The idea behind this is that in the highly correlated narrow band, s-wave pairing could well be repulsive. It is worth noting, further, that the superconductivity of these compounds must be thought of in different terms from that of the so-called re-entrant magnetic superconductors: for these latter, two separate weakly coupled electronic systems are in competition, while with the heavy-electron superconductors it is one and the same set of electrons which is deciding whether to be superconducting or magnetic.

In the presence of spin-orbit coupling, parity is the only obvious symmetry, and the superconducting state will have either even or odd parity. Among these states, the ones with essentially new properties will be those for which the gap possesses nodes on the Fermi surface, either points or lines where the gap vanishes. These should manifest themselves in non-exponential temperature variations in various properties below T_c, and a number of these have been seen. For example, $C = \gamma' T + \alpha T^3$ in UBe_{13} at very low temperatures [11]. The γ' term of 20 mJ/mole U-K^2, which is

sample dependent, can be rationalized as coming from the smearing out of points of the gap into finite areas due to impurity scattering, and it is known that the residual resistivity of good samples of UBe_{13} is some 10 to 20 $\mu\Omega$-cm. We note in passing that the slope of the upper critical field of UBe_{13} at T_c is at least 40 T/K (and perhaps infinite) [12].

The really surprising extra feature connected with UBe_{13} is the effect of Th impurities (Fig. 4). There is a negative cusp in T_c near 1.8 a/o Th [13]. Between this concentration and approximately 4 a/o Th there are two phase transitions [14]: the superconducting one and one near 0.4 K of unknown origin - perhaps to a second kind of superconducting state. Neutron scattering experiments [15] have detected no ordered magnetic moment in this state, and ^9Be NMR [16] has also found no sign of magnetic ordering. No other impurity has been found to cause this behavior. It is interesting that the value extrapolated for γ approximately doubles between $x = 0$ and $x = 3.3$ a/o Th. A few experiments have also involved substituting for Be in UBe_{13}: for B substitution, depressions in T_c are of approximately the same magnitude as seen for rare earth and Th impurities [17]. It also appears that there is no special extra depression associated with a magnetic moment on the impurity [13].

Further evidence for a new kind of superconducting state is the negative proximity-effect experiment of Han et al. (Fig. 5) [18]. In this experiment, conventional superconductivity is induced via the proximity effect in UBe_{13} with a Ta probe. Below the T_c of UBe_{13}, a depression of the Josephson critical current is found. The interpretation given is that the differing superconducting states of Ta and UBe_{13} are competing for electrons in a surface sheath. London penetration depth experiments [19] also provide evidence for a new superconducting state in UBe_{13}.

The present consensus, by no means unanimous, is that the superconducting states of UBe_{13} and UPt_3 are anisotropic with zeroes of the gap on the Fermi surface, and that either a p- or a d-type pair, loosely speaking, is involved. The possible mechanism is subject to considerable debate.

3. Magnetism

The low temperature normal state has been the subject of several neutron studies, in particular in the compounds UPt_3 [20], UBe_{13} [21], $CeCu_6$ [22] and U_2Zn_{17} [23]. For the first three, strong magnetic fluctuations are found with characteristic energies of some tens of wavenumbers, with $\chi(q)$ peaking near a zone boundary for temperatures below the coherence temperature.

U_2Zn_{17} [24] and UCd_{11} [25] order magnetically at $T_N = 9.8$ K and 5 K respectively. Although the phase transition in U_2Zn_{17} bears some qualitative resemblance to a BCS-type transition (Fig. 6), this comparison does not hold up in detail, although entropy is approximately conserved through it. The ordered moment on U in U_2Zn_{17} is 0.8 μ_B, considerably smaller than the effective Curie-Weiss moment of approximately 3.3 μ_B. It is interesting that the square of the ratio of the ordered moment to the effective moment gives roughly the relative loss of γ upon ordering. Spin waves have been looked for below T_N in U_2Zn_{17} and not found [26] - this could possibly be similar to the Cr case where the spin waves are believed to travel with the Fermi velocity.

Another interesting and somewhat different heavy-electron antiferromagnet is UCu_5. A simple, antiferromagnetic order is observed below T_N = 15 K with ordered moment of 0.8 μ_B [27]. Below 3 K, however, C/T shows an upturn and a second phase transition occurs at 1.0 K [28]. Impurities suppress this lower transition, and it is clear that a heavy-electron state is developing within the ordered magnetic state below T_N = 15 K.

4. Comments

It might be expected from the high temperature properties of the heavy-electron compounds that they would order magnetically upon cooling. In fact, only a few of them do. We show in Table 2 that the low temperature phase transitions for U-compounds seem to be ranked according to γ_V, the γ per unit volume. It is clear that the superconductors have larger γ_V's than the magnetically ordering compounds. Experiments show that γ for UBe_{13} is strongly depressed by hydrostatic pressure, 30% at 6 kbar [29], while χ changes roughly 10% at this pressure [30]. This suggests that sufficiently high pressure could cause magnetic order to appear in UBe_{13}, a counter-intuitive notion.

The heavy-electron compounds which order magnetically lie further from the Sommerfeld free-electron line in Fig. 2 than the superconductors do. Speaking loosely, the magnets are less efficient than the superconductors in converting local moment entropy into conduction electron entropy. Experiments measuring the specific heat of U_2Zn_{17} and $CeCu_6$ [31] to fairly high temperature find, in this regard, that an integrated entropy for the electronic system of Rln6 per mole Ce is achieved by 70 K in $CeCu_6$, whereas U_2Zn_{17} has something quite a bit in excess of Rln10 per mole U by this temperature. The first number is exactly that expected for the J = 5/2 Ce Hund's Rule ground state; the U_2Zn_{17} value is anomalous. A possible source for this extra entropy could be, one imagines, an extra degree of freedom derived from the conduction electrons via hybridization with the U f-electrons.

Strong effects of impurities on magnetic ordering have been observed for Cu substitutions in U_2Zn_{17} [32] and Ni in UCu_5 [33]. T_N disappears with small additions in both cases. This is not a simple dirt sensitivity; it depends, we are now finding, on impurity valence, among other things. We also now know that a number of additions (Th, Au, Pd) to UPt_3 at the 5% level lead to magnetic ordering [34]. It is peculiar in this case that the ordering observed has a structure in k-space significantly different from the structure observed in $\chi(q)$ for pure UPt_3 [35].

Nothing has been said in this short summary concerning theoretical attempts to treat the ordered lattice of f-atoms in these compounds. Anderson lattice models have been investigated, but as yet there is very little certainty about what is happening in detail as coherence develops [36]. It is surprising that Oguchi and Freeman [37] seem to get results in rough agreement with the de Haas-van Alphen measurements on UPt_3. The effective masses, of course, turn out to be completely wrong, but the idea is that a proper many body theory applied to the band structure results would give something reasonable. This approach has not been successful as yet.

UPt_3 has been quite extensively attacked via Fermi liquid theory [38], UPt_3 seeming to have the right low temperature resistivity and specific

heat behavior for the theory. The large anisotropy in χ of UPt_3 is clearly something of a problem for this theory. For UBe_{13}, the Fermi liquid regime is presumably at a much lower temperature, and the superconducting transition is reached before the coherent state is achieved. This makes the Fermi liquid approach to the superconductivity of UBe_{13} less appropriate.

A final point to make about the physics of the heavy-electron materials is that it appears to be dominated by spin fluctuations. In transition metal magnetic materials, both charge and spin fluctuations are important. The heavy-electron materials, therefore, represent a projected piece of the more general transition metal problem, and it is to be expected that what we learn from the heavy-electron compounds can throw new light on transition metal materials.

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Figure Captions

Fig. 1. C/T versus T^2 for UBe_{13}. Inset shows the anomaly in C at T_C.

Fig. 2. Lnγ versus lnχ for U compounds. The line is the free electron relationship.

Fig. 3. Hall coefficient of $CeCu_6$. Data from ref. 1.

Fig. 4. Variation of T_C for U_{1-x} Th_x Be_{13} alloys.

Fig. 5. Comparison of Josephson critical currents observed in Mo-Ta and UBe_{13} - Ta junctions. From ref. 18.

Fig. 6. Electronic specific heat of U_2Zn_{17} through T_N. C^{el}/T versus T is plotted. Solid line is curve calculated with a BCS-type model. C^{el}/T is per formula unit.

Table 1. Some Heavy-Electron Compounds

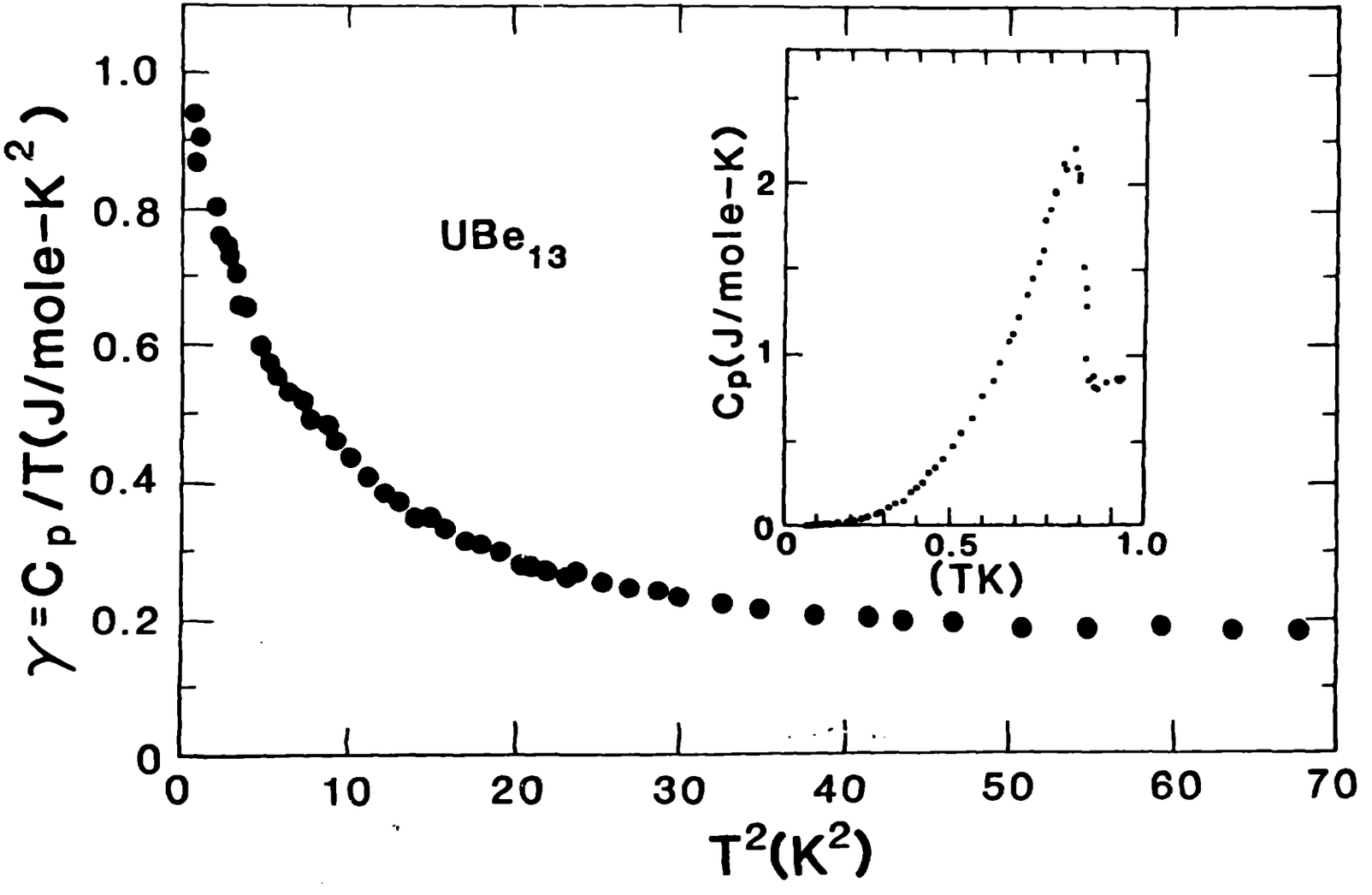
Compound	γ*(mJ/mole f-K^2)	ordering**
$CeCu_2Si_2$	1200	s, T_s = 0.6 K
$CeCu_6$	1600	n
$CeAl_3$	1500	n
UAl_2	150	n
UPt_3	450	s, T_s = 0.54 K
U_2Zn_{17}	535	m, T_N = 9.8 K
UCd_{11}	840	m, T_N = 5.0 K
$UAuPt_4$	725	n
UBe_{13}	1100	s, T_s = 0.9 K

*γ extrapolated from above T_N for magnetically ordering materials.
**s ≡ superconducting
m ≡ magnetically ordering
n ≡ not ordering

Table 2. Electronic Specific Heats per Mole-U for Various U Compounds

Compound	γ(mJ/mole-K^2)	γ_V(mJ/cm^3-K^2)	Ordering*
α-U	12	0.96	s
UPt_5	85	1.38	n
URu_2Si_2	75	1.52	m, s
U_2PtC_2	75	1.59	s
UIr_2	52	1.63	n
URu_4B_4	170	1.63	n
U_6Fe	25	1.79	s
$U_2Co_3Si_5$	115	2.55	n
USn_3	169	2.84	n
UCu_5	210	4.03	m
UAl_2	150	4.25	n
U_2Zn_{17}	500	5.08	m
UCd_{11}	840	5.21	m
UPt_3	450	10.59	s
$UAuPt_4$	725	11.7	n
UBe_{13}	1180	13.55	s

*n = no ordering, m = magnetic ordering, s = superconducting.


$\gamma = C_p/T$(J/mole-K^2)
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0.8
0.6
0.4
0.2
0
UBe$_{13}$
0
10
20
30
40
50
60
70
T^2(K^2)
C_p(J/mole-K)
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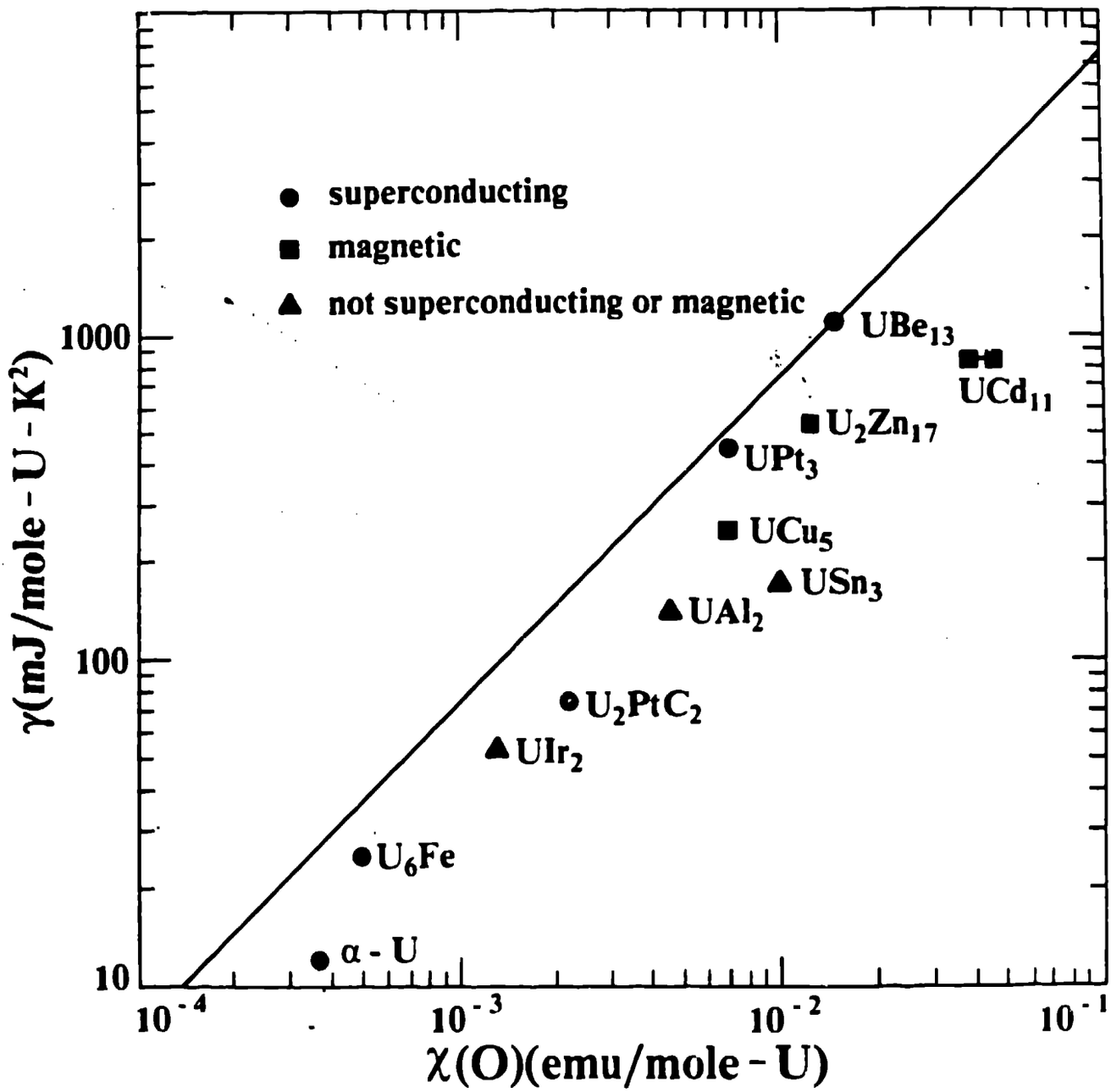
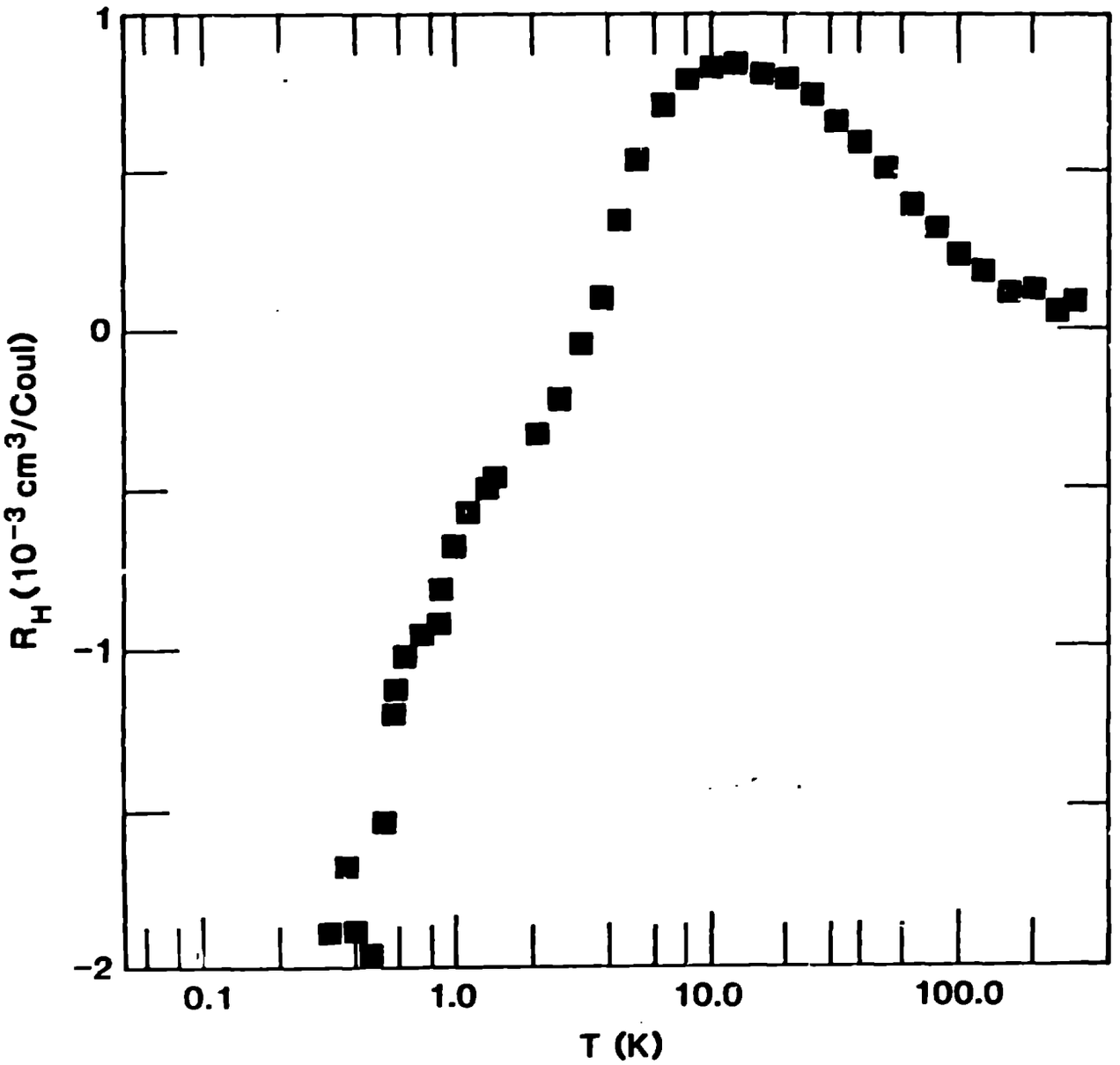
1
0
0
0.5
1.0
(TK)


superconducting
magnetic
not superconducting or magnetic
UBe13
UCd11
U2Zn17
UPt3
UCu5
USn3
UAl2
U2PtC2
UIr2
U6Fe
α - U
1000
100
10
γ(mJ/mole - U - K²)
10⁻⁴
10⁻³
10⁻²
10⁻¹
χ(O)(emu/mole - U)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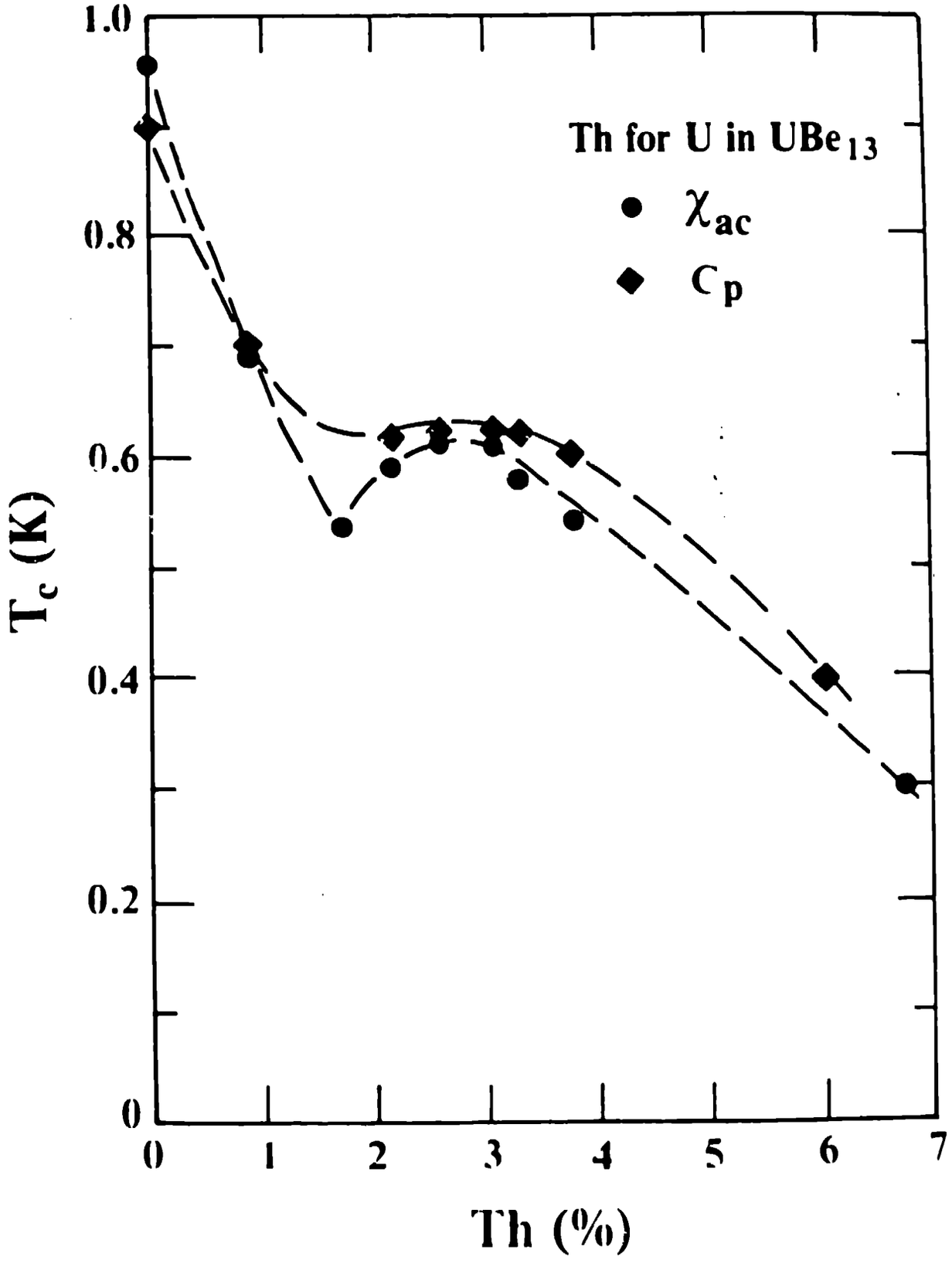
1.0
10.0
100.0
T (K)


Th for U in UBe13
χac
Cp
Tc (K)
Th (%)
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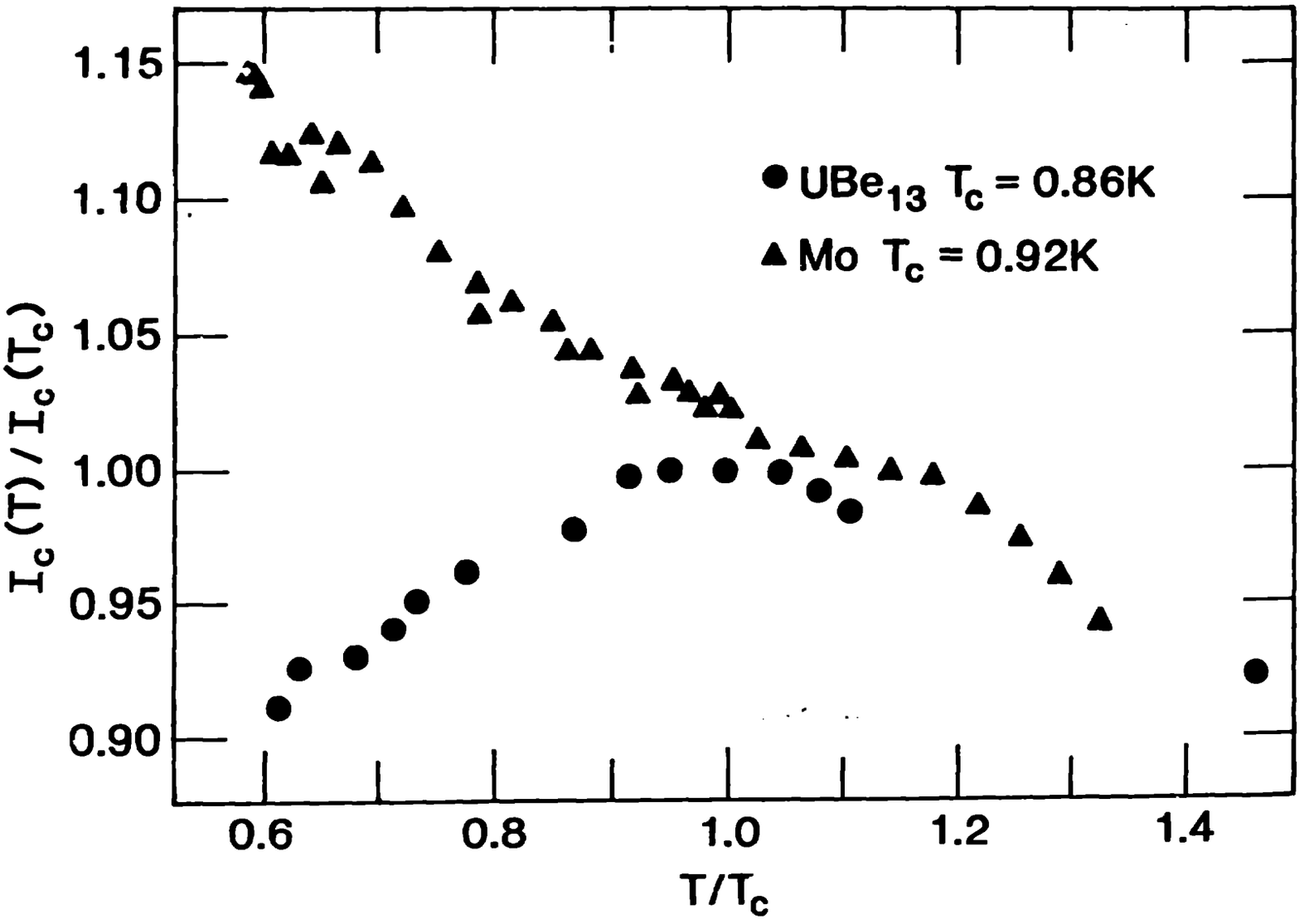
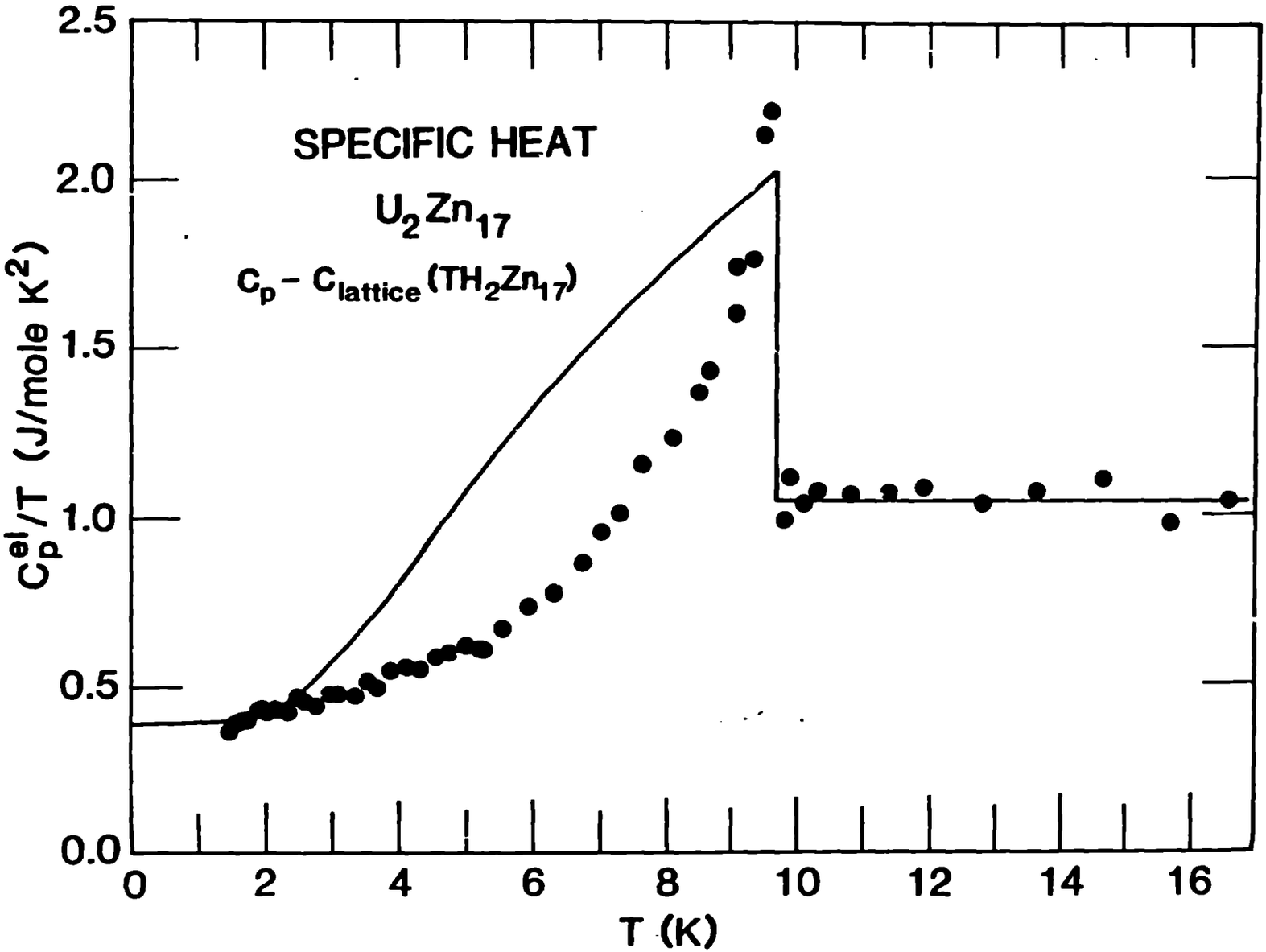
0.4
0.2
0
0
1
2
3
4
5
6
7


1.15
1.10
1.05
1.00
0.95
0.90
$I_c(T) / I_c(T_c)$
0.6
0.8
1.0
1.2
1.4
T/T_c
● UBe_{13} T_c = 0.86K
▲ Mo T_c = 0.92K


SPECIFIC HEAT
U_2Zn_{17}
$C_p - C_{lattice}(TH_2Zn_{17})$
C_p^{el}/T (J/mole K^2)
T (K)
2.5
2.0
1.5
1.0
0.5
0.0
0
2
4
6
8
10
12
14
16